Highly active screen printed Ir-Ti_4O_7 anodes for proton exchange membrane electrolyzers

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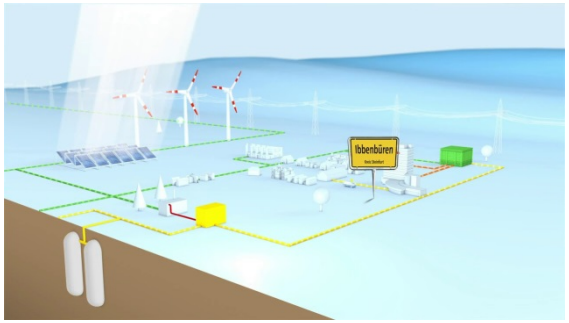
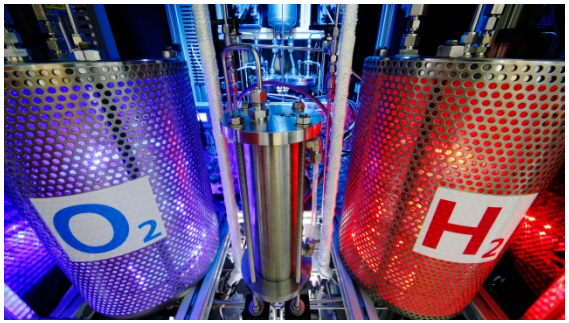
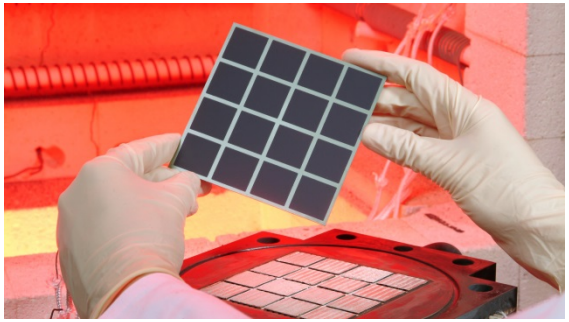
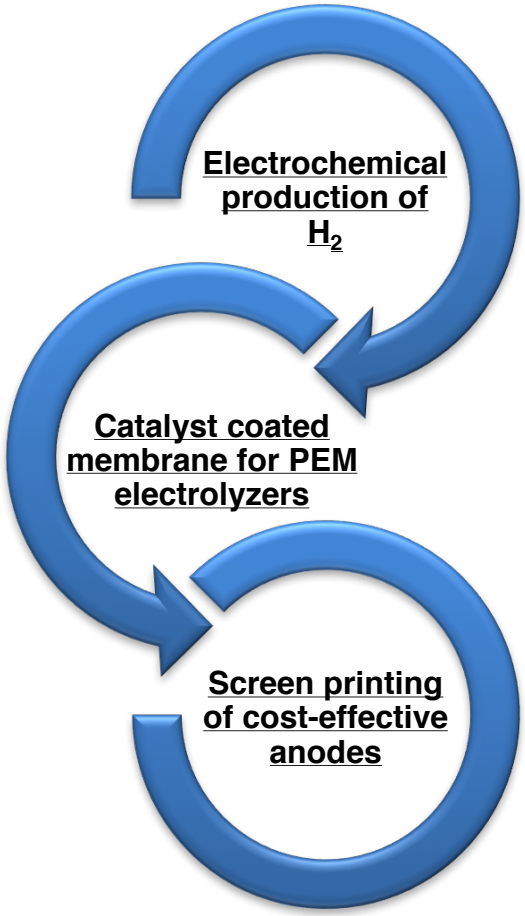
DLR

Motivation: a contribution towards implementation of a H_2 society







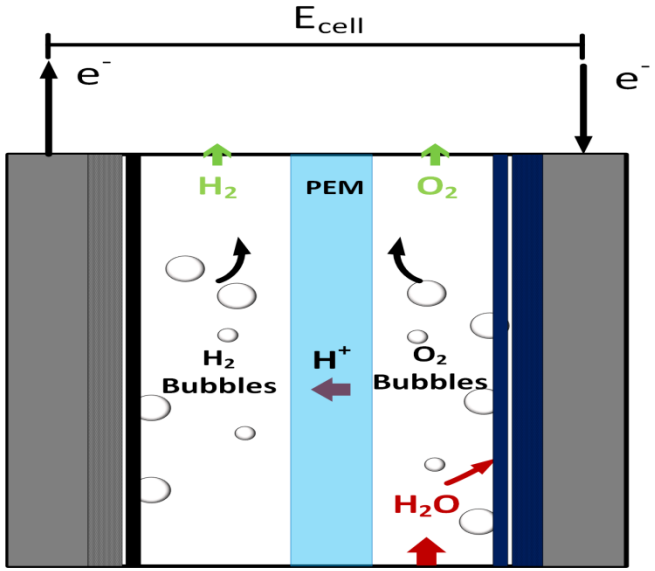


- Power-to-gas concept
- Carbon neutral energy vector
- Zero-emissions energy cycle

- High purity (99.995 %)
- High current densities (> 2 A cm^{-2})
- Operation at high pressure

- Cheap and easy-scalable technique
- Corrosion-resistant catalyst support
- Low loading of precious metal

Electrolyzer components



Cell requirements:

- **Proton conductive membrane**
  >>> Nafion
- **Cathode material**
  >>> similar to PEMFC
- **Anode material**
  >>> Corrosion resistant
  >>> Iridium as catalyst

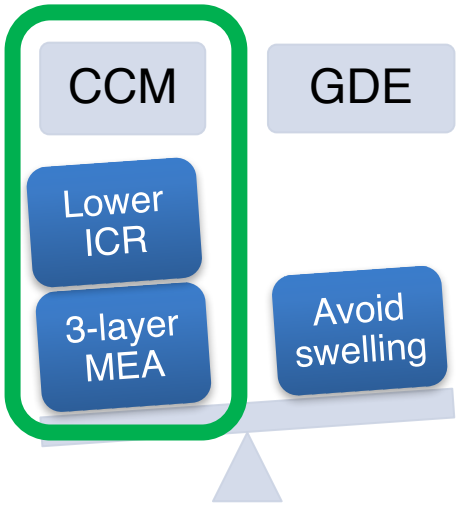
	Anode catalyst	Cathode catalyst	Anode loading (mg cm^{-2})	Cathode loading (mg cm^{-2})	Anode CC	Cathode CC	Cell temperature (°C)	E (V) @ 1 A cm^{-2}	Coating method
1	IrO_2	40%Pt/C_{JM}	1	0.2	C Cloth	C Cloth	80	1.64	Decal
2	Ir Black	40%Pt/C_{XC72}	1	0.8	SPT	SPT	90	1.7	-
3	Ir Black	Pt	2.5	1	SPT	SPT	90	1.79	S-SPT
4	IrO_2	30%Pt/C_{TKK}	1.5	0.5	C Toray	C Toray	80	1.67	S-Mem
5	Ir Black	Pt Black	2	0.8	Pt/SPT	Pt/SPT	90	1.71	S-SPT

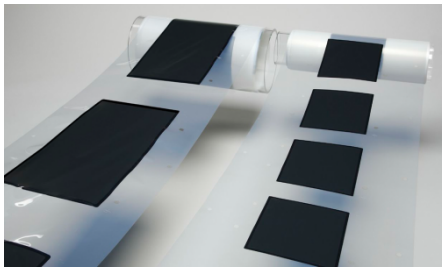
Abbreviations: TKK=Tanaka Corp.; JM=Johnson & Matthey; SPT=sintered porous titanium; C=carbon; S=sprayed catalysts; Mem=membrane; CC=current collectors.

Adapted from Carmo et al, *International Journal of Hydrogen Energy* **38,** 4901–4934 (2013)

Membrane Electrodes Assembly

Technical approach





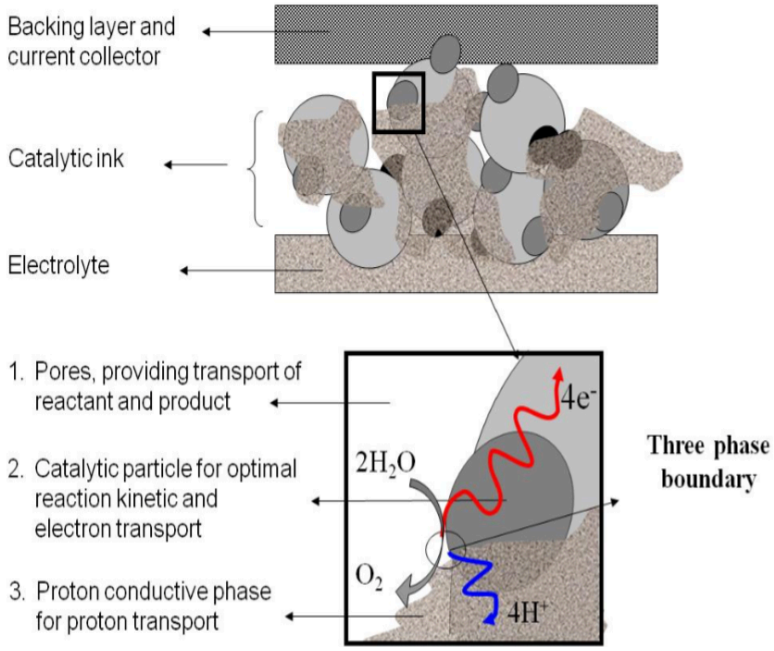


Illustration of the three phase boundary system - www.intechopen.com, 2015.

Catalyst layers:

- **Low cost scalable manufacturing:**

  >>> screen printing

- **High ECSA**

  >>> Catalyst + Ionomer + Electronic Conducting Phase

- **Low precious metal loadings**

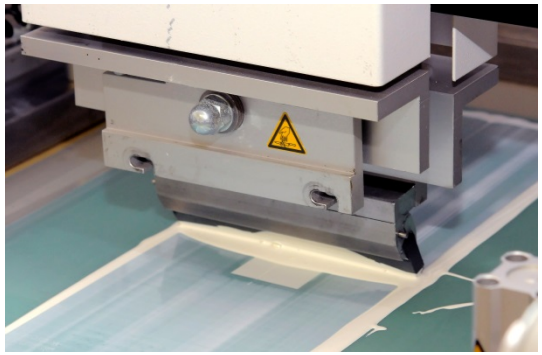
  >>> Supported catalyst: Ir on Ti_4O_7

Screen printing paste formulations

Paste formulations	Catalyst (7.875 wt%)	Catalyst Support (18.375 wt%)	Binder (11.25 wt%)	**Solvent (62.5 wt%)**
A	Ir Black	Ti_4O_7*	Nafion ionomer	**Ethane-1,2-diol**
B	Ir Black	Ti_4O_7*	Nafion ionomer	**Propane-1,2-diol**
C	Ir Black	Ti_4O_7*	Nafion ionomer	**Cyclohexanol**

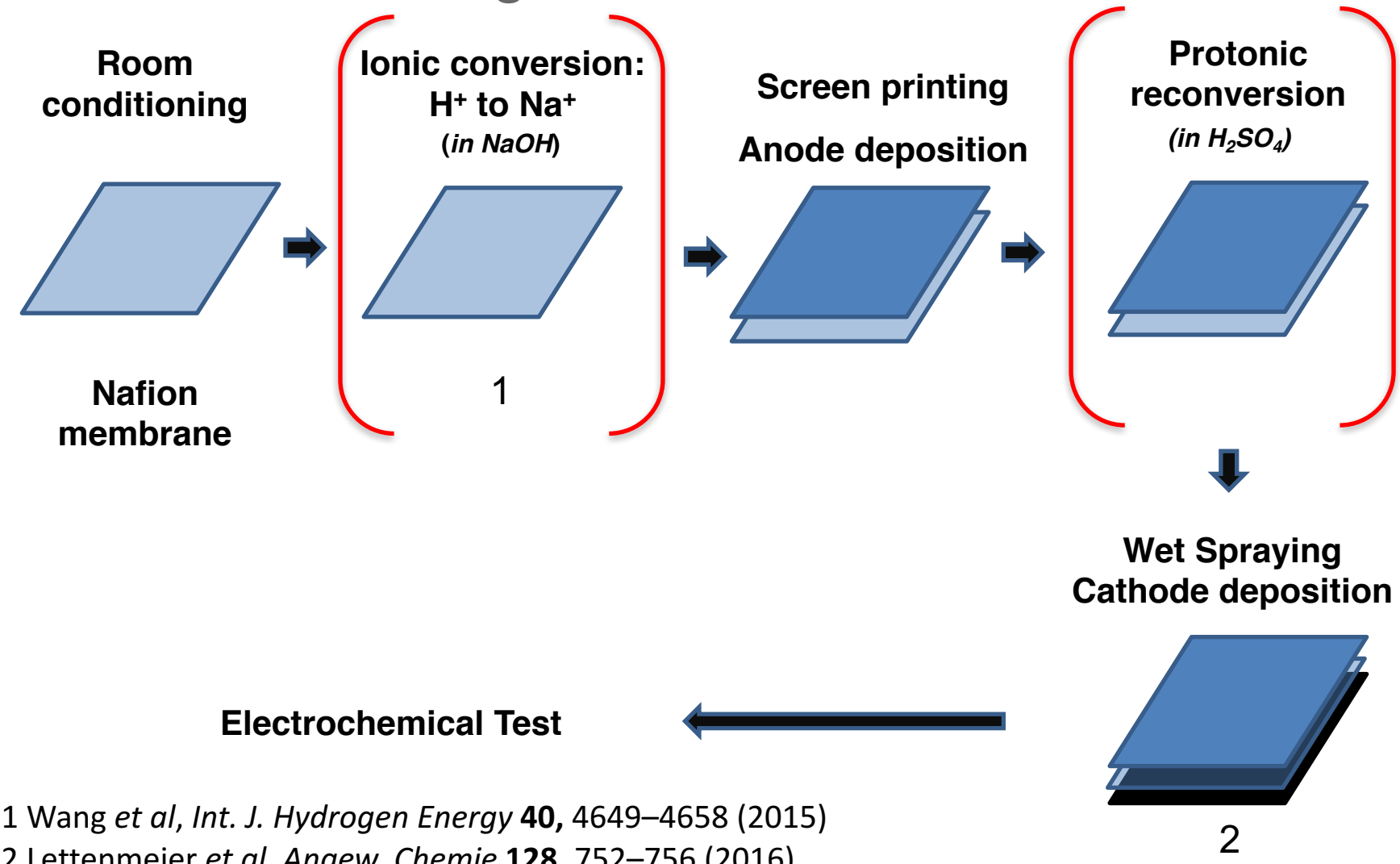
Solvent choice criteria:

- **Viscosity**
- **Evaporation rate**
- **Relative permittivity**



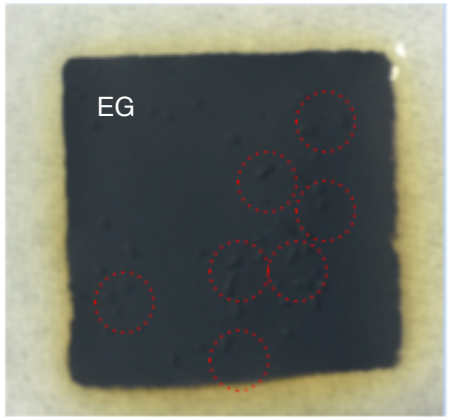
*Wang et al, *Phys. Chem. Chem. Phys.* **18,** 4487–4495 (2016).

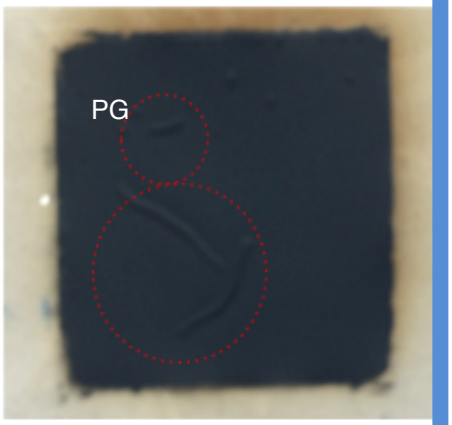
CCM Manufacturing route

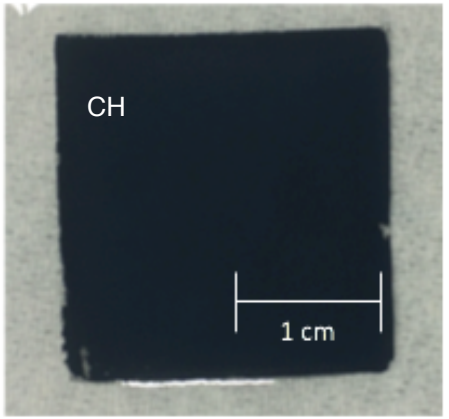


1 Wang *et al*, *Int. J. Hydrogen Energy* **40,** 4649–4658 (2015)
2 Lettenmeier *et al*, *Angew. Chemie* **128,** 752–756 (2016).

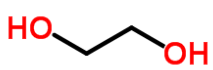
Screen printed anodes

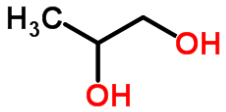


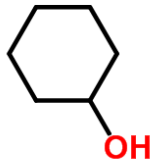


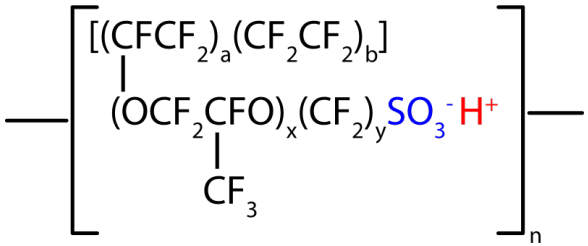


Thickness: 13 μm



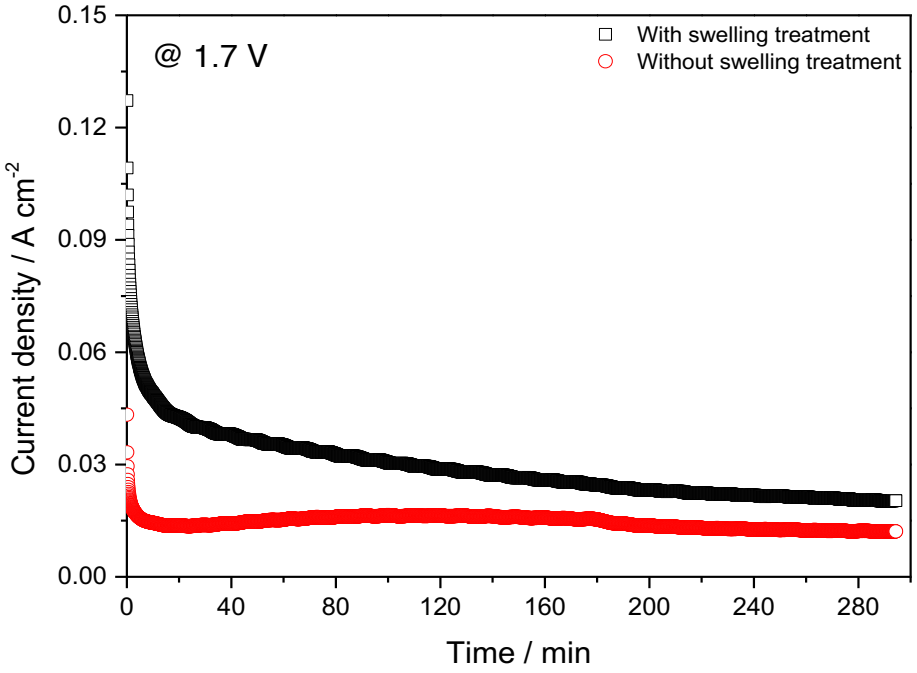


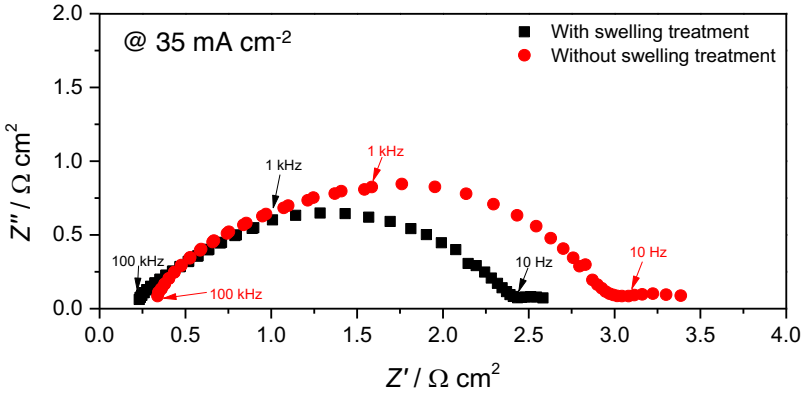


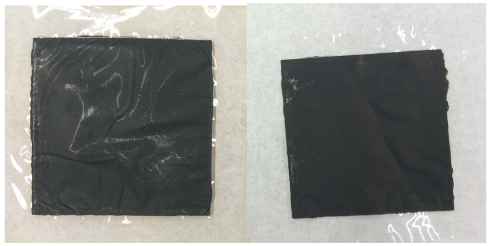


No membrane swelling!

Effect of swelling treatment:
paste with ethane-1,2-diol

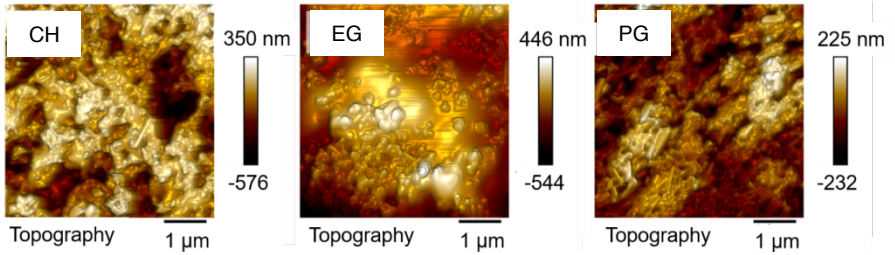


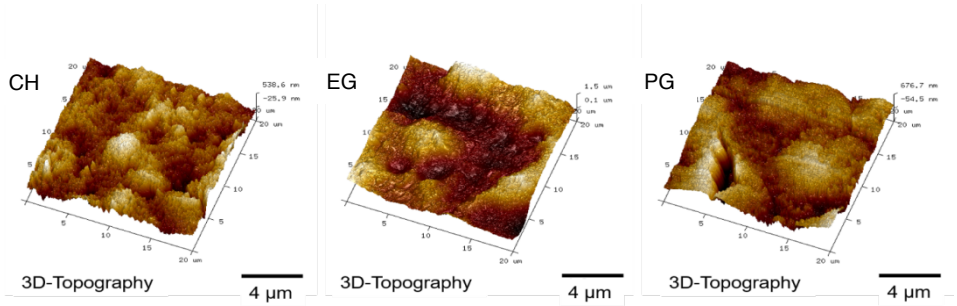




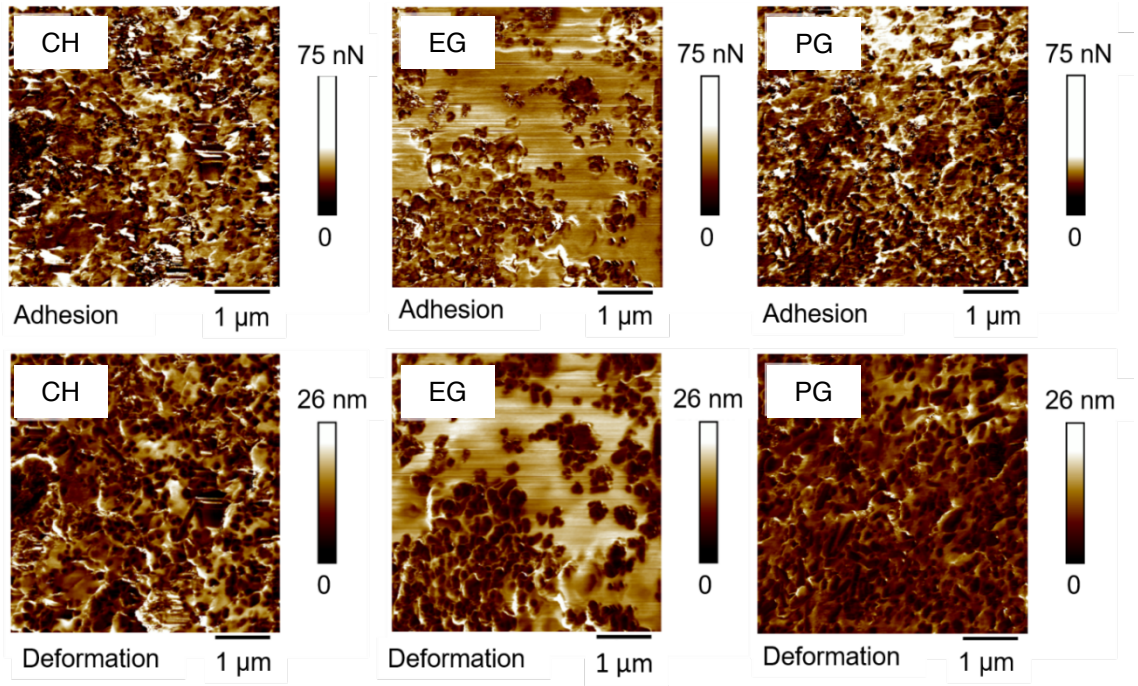
Not harmfull for proton conductivity!

Post-mortem AFM analysis

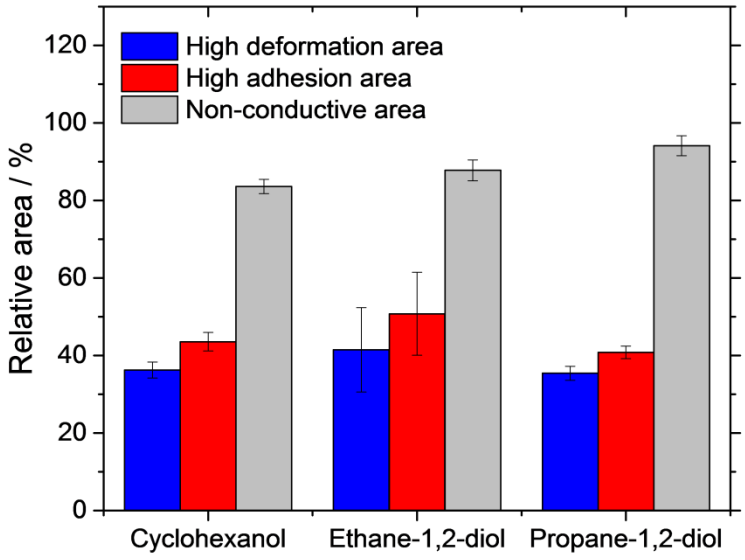


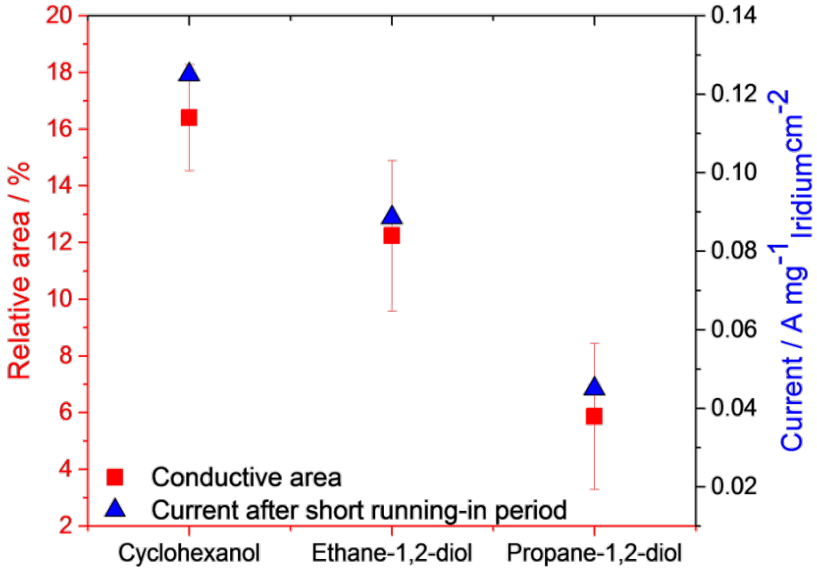


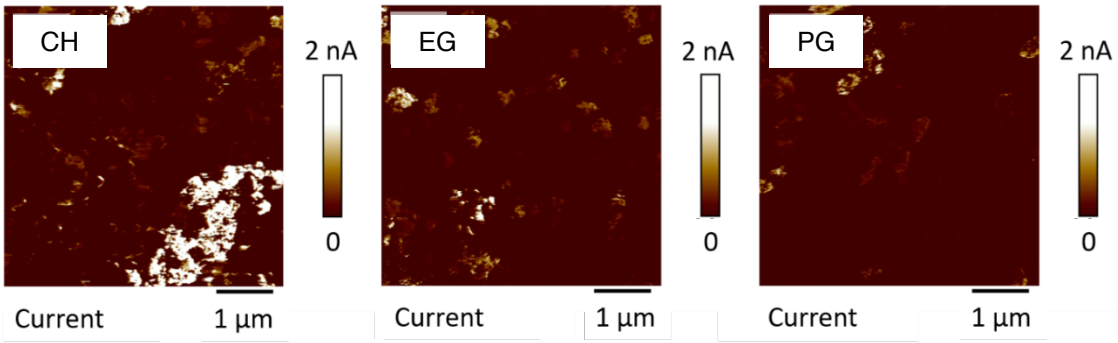
Best ionomer/Ir-Ti_4O_7 Distribution was achieved with anode coated with cyclohexanol



AFM – conductivity measurements





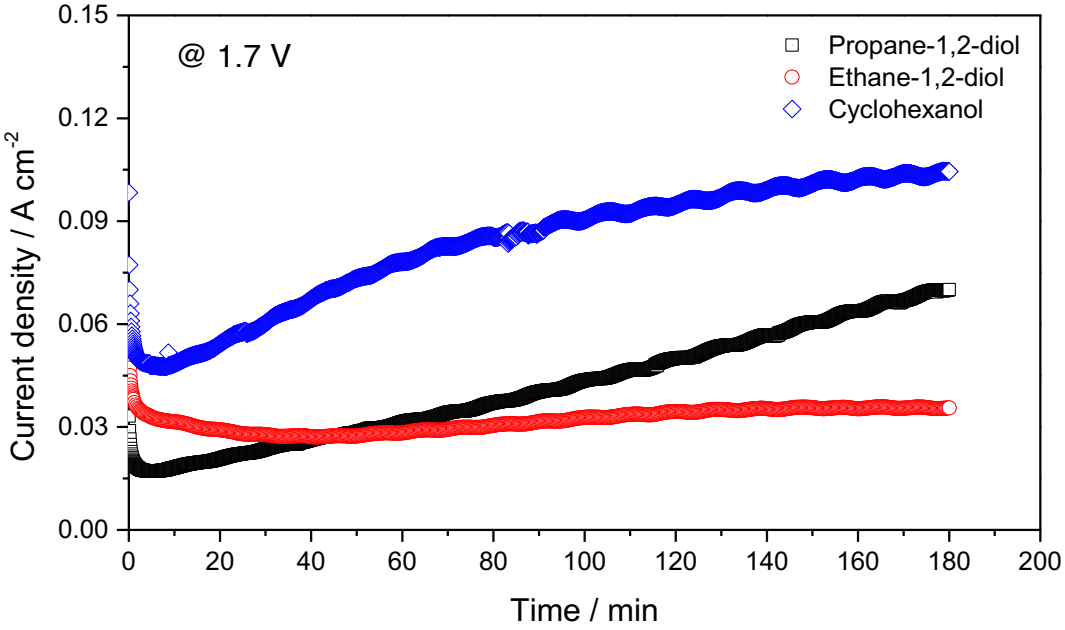


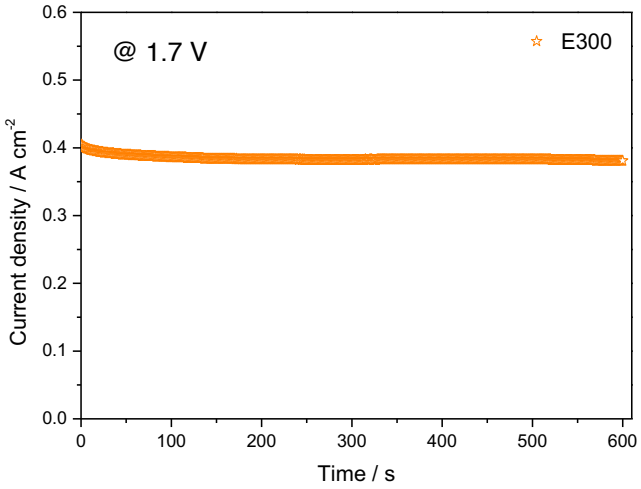
Lower ionomer/Ir-Ti_4O_7 ratio would increase electronic conductivity

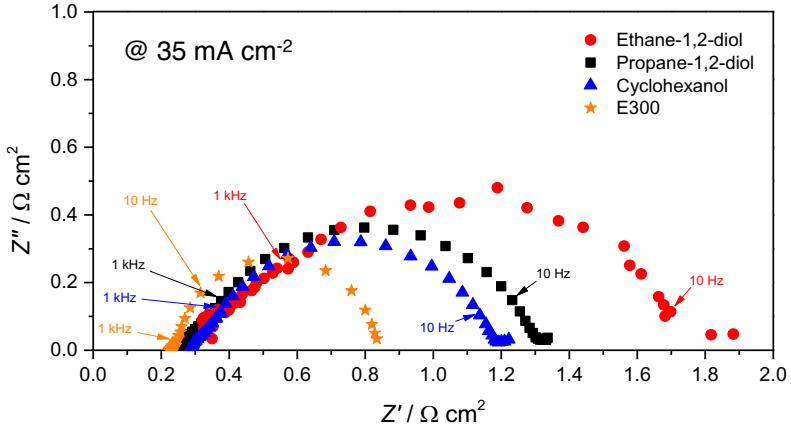
>>> increase of activity?

Eletrochemical measurements

Chronoamperometry and EIS





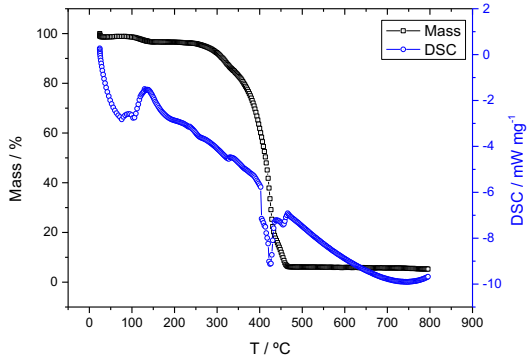


Need for CCM "break-in"

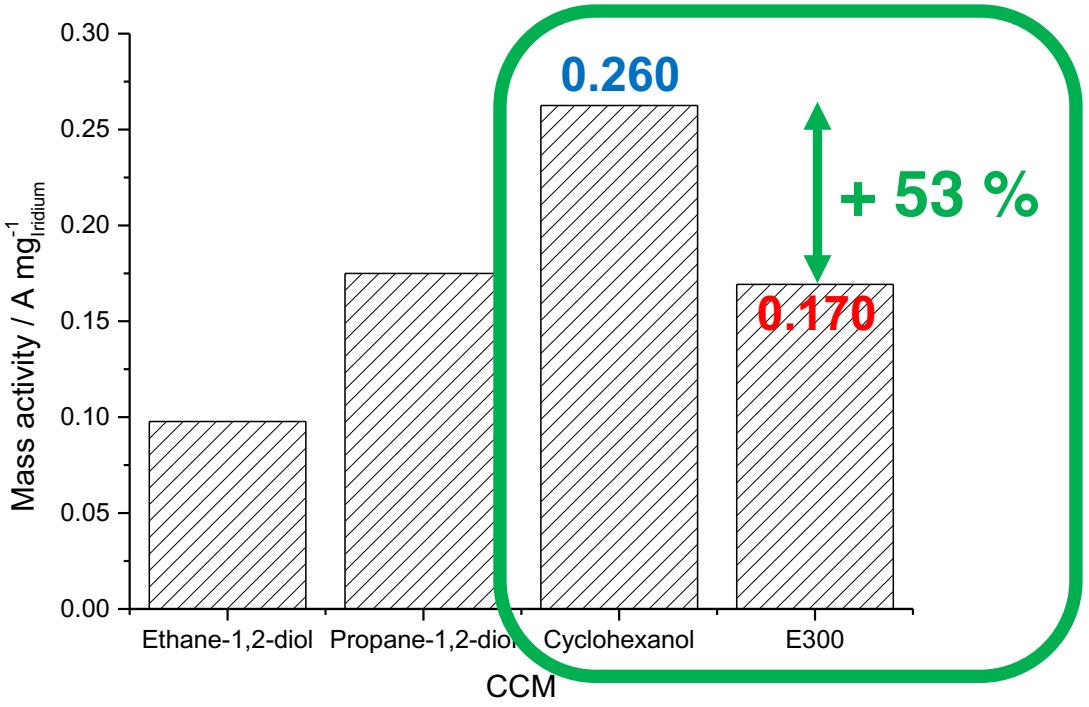
Ir loadings and Ir mass-activities

***Screen Printed* MEA: catalyst loading:**

- **Mass difference: 0.4 mg_{Ir} cm^{-2}**
- **Method validation with TGA: 0.42 mg_{Ir} cm^{-2}**
- **Cathode loading: 0.5 mg_{Pt} cm^{-2}**



Commercial Reference (E300): 2.25 mg_{Ir} cm^{-2}



Conclusions

- **CCMs with catalyst loading as low as 0.4 mg_{Ir} cm^{-2}** were successfully fabricated by screen printing;
- Swelling treatment was effective, without hindering CCM performance;
- **A decrease of ionomer content could lead to a higher electrochemical performance;**
- Cyclohexanol was found to be a suitable single solvent for coating anodes directly on the membrane;
- The **screen printed CCM** using cyclohexanol as ink vehicle delivered the highest Ir-mass activity of **0.26 A mg^{-1} at 1.7 V** and 40 ºC, which is approx. **53 % higher** than that of the commercial reference CCM (Greenerity E300).

Acknowledgements

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Thanks for your attention